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Development and Characterization of Bismaleimides Containing Aliphatic Chain for Microelectronics Application

J. L. Feng, C. Y. Yue and K. S. Chian*

School of Mechanical & Aerospace Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798; Fax 65-67934637; p147049664@ntu.edu.sg

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Abstract: A series of bismaleimide systems containing aliphatic backbone chain have been synthesized and investigated. Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Thermomechanical analysis (TMA), rheometry and tensile test were used to characterize the thermal and mechanical properties. It was noted that backbone chain length and odd-even effect affected properties. As the chain length increases, the curing peak temperature, gel temperature of BMI all increase, but the melting point, glass transition and moisture absorption decrease. The melting points of BMI-3,5,7 reduced most significantly. The tensile properties were affected by odd even effect significantly. BMI-3,5,7 with odd number of carbons have less stress and strain than those of even ones.

Introduction

Thermoset bismaleimide (BMI) has been widely applied in microelectronic application such as multi-layered printed circuit boards because of their excellent thermal, mechanical and electrical properties and a comparatively low dielectric constant about 3.5 [1, 2]. BMI resins have 'epoxy-like' processing characteristics, while they exhibit higher glass transition temperature than epoxies [3]. Typically, dielectric constants of electronics packaging material should be low (between 2.0 and 3.5) over a very wide frequency range [4, 5]. The conventional polyimide resin and bismaleimide-based cured resin have high dielectric constant i.e. 3.4 or higher. Since BMI contains two reactive double bonds, the cured network is very brittle due to the high cross-linking density and aromatic nature. One approach to improve its toughness is to introduce the flexible and longer backbone main chain between two maleimide rings. Most investigations were focused on aromatic BMIs with two phenyl groups. In our study, the BMI includes only -CH_2- repeating unit which is a non-polar and flexible group. The dielectric constant of the polymer can be calculated by the Clausius-Mossotti equation [6]. It was expected that a low dielectric constant could be achieved by having repeating units with low polarity and low polarizability. Because the low polarity of aliphatic group and low polarizability of the C–F bonds result in low dielectric constants of polymers, the incorporation of aliphatic group and fluorine substituents into polymer materials are two effective approaches to decrease the dielectric constant. This paper will study the modified BMI containing aliphatic chain as backbone.

Results and discussion

DSC analyses of bismaleimides (BMIs)

The thermal and cure behaviour of all the BMI samples were investigated by DSC. The obtained products exhibited one endothermic peak (T_m) due to the melting and one exothermic peak (T_p) due to the curing reaction. The initial thermal curing temperature is the onset temperature (T_o) of the exothermic peak.

The varying trends of melting point, curing temperature of BMI systems are displayed in Figure 1. It can be seen from Figure 1 that, in general, BMI systems having longer flexible -CH_2- groups have lower melting points. This is because the chain flexibility and intermolecular cohesive force has a significant effect on the melting point. As the chain length increases, increasing flexible linkages between the two maleimide rings and the decreasing density of polar groups lead to a decrease in the melting point.

However, the melting temperatures of BMI-3, BMI-5 and BMI-7 with odd carbon chain decrease more significantly than that of BMI-2, BMI-4, BMI-6 and BMI-8 with even carbon chain. This indicates that the melting temperatures follow an odd-even chain-length effect. When CH_2 length is odd, the packing density is lower. So an even number of carbons on the main chain normally results in higher melting temperatures. BMI-3, BMI-5 and BMI-7 have odd number of carbons so that their melting points reduced most significantly.

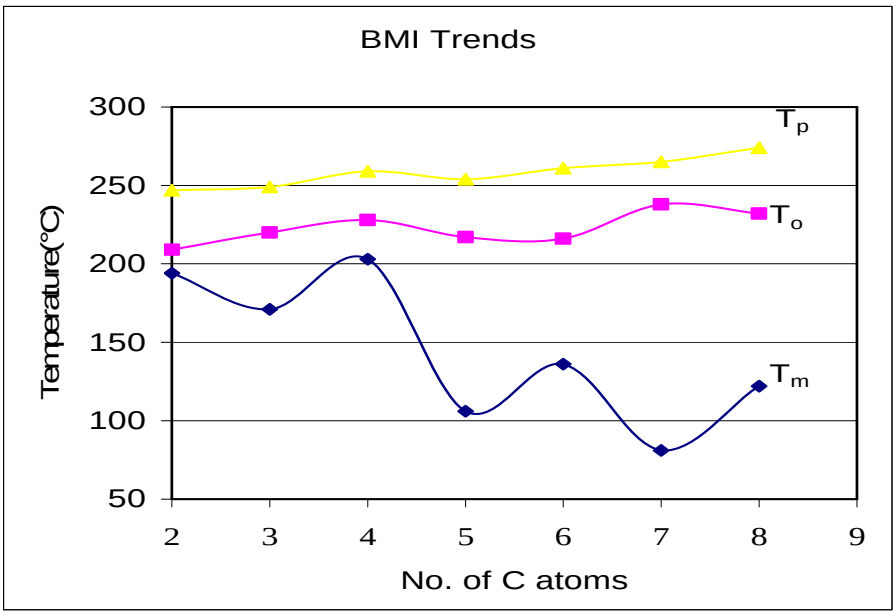


Fig. 1. The effect of chain length on melting points and curing temperatures.

It is observed from Figure 1 that the polymerization onset temperatures (T_o) and peak temperatures (T_p) of these BMIs increases with chain length increase. That is to say that the exotherm peak is shifted to a higher temperature as the backbone chain length increases.

Gelation point

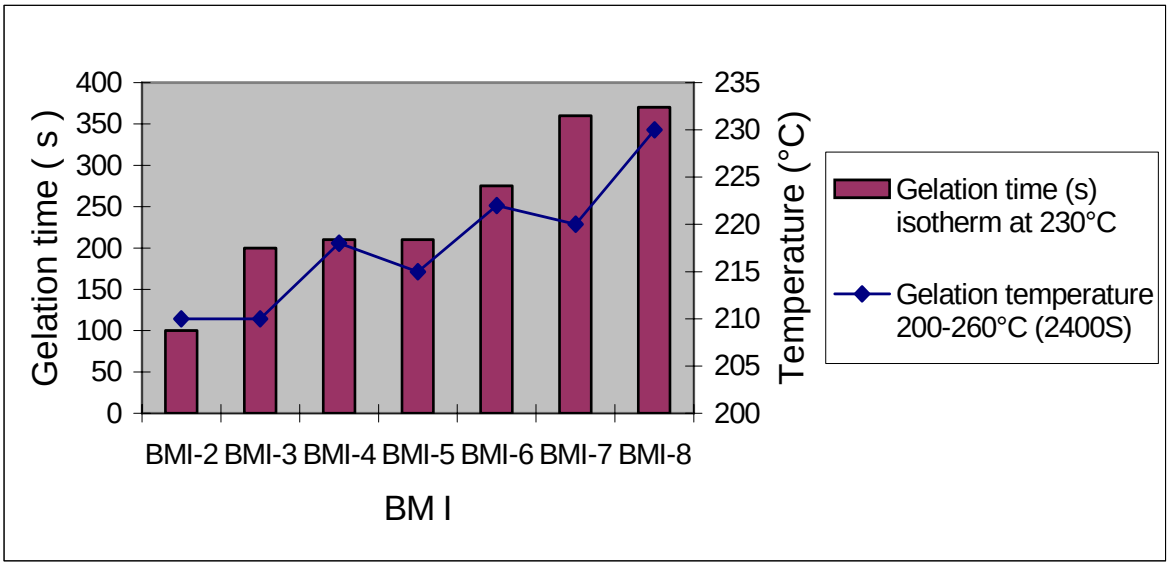


Fig. 2. The varying tendency of gelation point.

Gelation temperatures and gelation times were found to increase with chain length of BMI monomer increasing as shown in Figure 2. As the chain size increases, BMI should be more stable since the chain length increase, resulting in an increase in the gelation temperatures and gelation times. There is also a big fluctuation for gelation temperature due to odd-even effect as the main chain length increases. This indicates the reactivity is affected by the odd even effect.

Thermal decomposition of BMI

All the BMI systems showed onsets of degradation at approximately 450°C in dry air and in pure nitrogen as displayed in Figure 3.

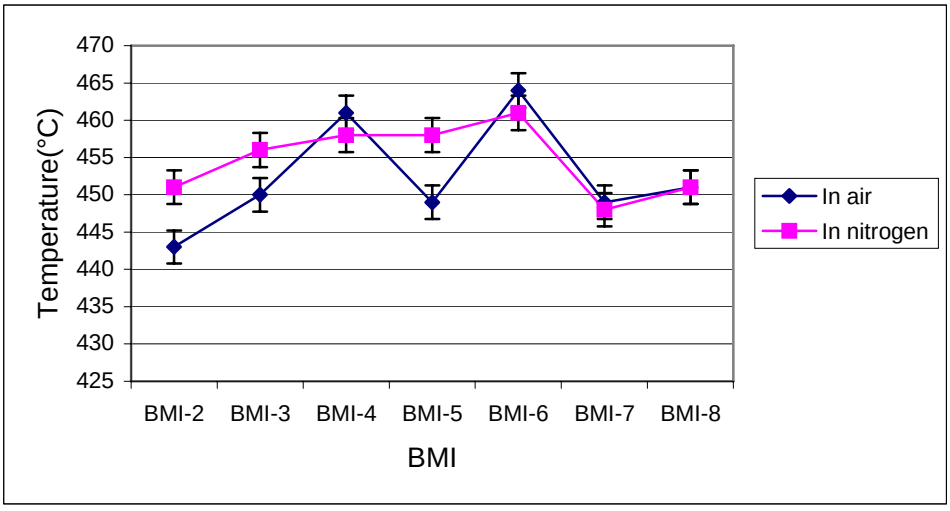


Fig. 3. TGA thermal degradation on cured BMIs.

Thus increasing the number of aliphatic C atoms on the backbone chain appears to increase the thermal stability first and then lower the thermal stability slightly. The decomposition temperatures of these BMIs under air have a bigger fluctuation than those under nitrogen, which implies BMI-5,7 are sensitive to thermooxidative degradation due to loose packing. The looser packing is easier for oxygen diffusion. The thermal degradation is caused by the cleavage of the C-C linkage close to maleimide ring because alkylene linkages are least stable linking units compared with other groups such as -O-,-S-and –CO- [7]. The density of weak bond C-C close to maleimide ring decreased for the cured BMIs as the backbone chain length of BMI increases. So the cured BMI-2 has more weak bonds than those of the cured BMI-6, which leads to lower thermal degradation temperature for BMI-2. While BMI-8 shows a low T_d due to loose packing and more free volume.

Glass transition temperature and CTE of bismaleimides

Figure 4 showed TMA varying trends of cured bismaleimides. T_g for BMI-3~8 are around 388-413 °C, with a slight decrease with chain length increase. This temperature was not observed for BMI-2 indicating that the glass transition temperature is above its decomposition temperature. Final T_g of BMIs appears to be slightly affected by the number of aliphatic carbon atoms in the chain. The CTE values for bismaleimides increased significantly with chain length increase. It is reasonable that the introduction of long chain into two maleimide groups will decrease its cross-link density and increase free volume of the cured sample, thus decrease the T_g and increase the thermal expansion coefficient. Odd-even effect also affects the glass transition temperature and CTE as shown in Figure 4, BMI-3,5,7 have a lower glass transition temperature and a higher CTE than those of BMI-4,6,8 respectively due to looser packing.

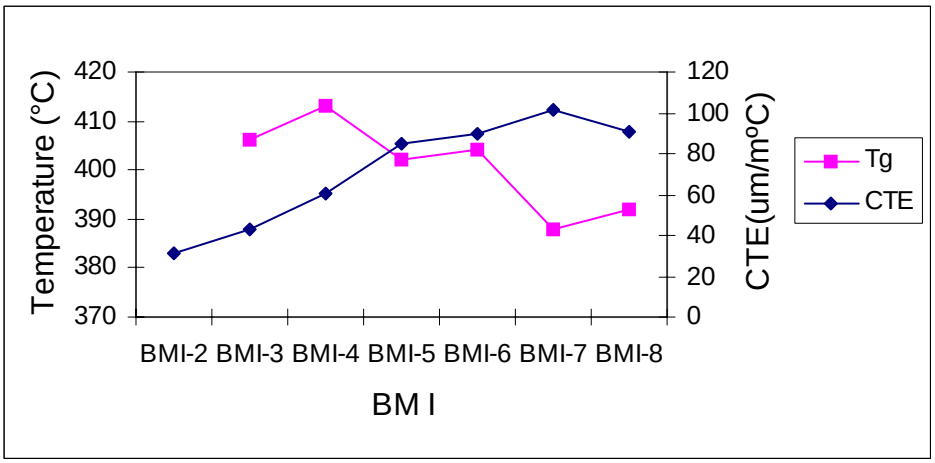


Fig. 4. The varying trends of T_g and CTE of cured BMIs.

Tensile properties

This section summarizes the effect of the molecular structure on the tensile properties of various samples. Figure 5 shows a typical stress-strain curve of the pure BMI specimen. The tensile modulus of the sample is calculated from the slope of the linear portion of the stress-strain curve.

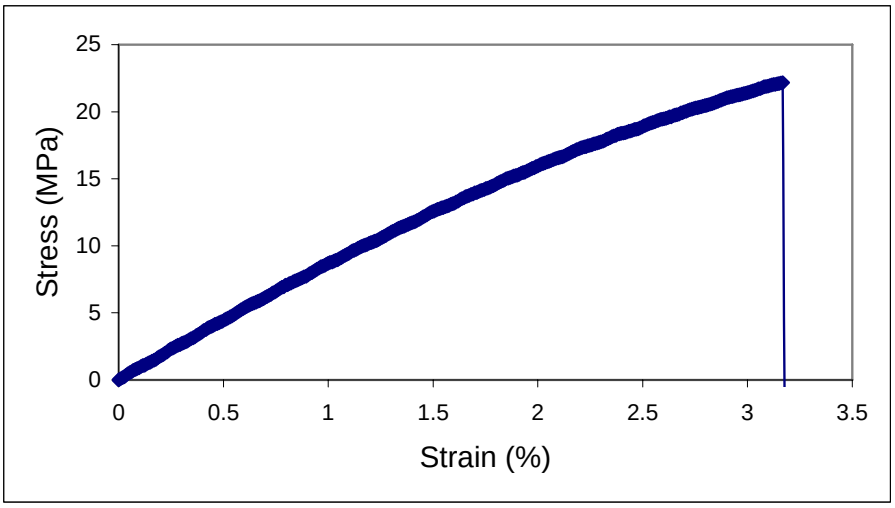


Fig. 5. A typical stress-strain curve of the BMI sample.

From Figure 6, it is interesting to observe that tensile stress, strain and modulus increases with increasing carbon chain at first, and then decreases gradually. The observed enhancement in stress and strain for BMI-2,3,4 could be due to the incorporation of flexible longer chain within the thermosetting network which enhances its ability to be deformed. Short chains show the effect of limited elongation on the strength and Young's modulus of cross-linking net works. The short chains deform less than their counterparts.

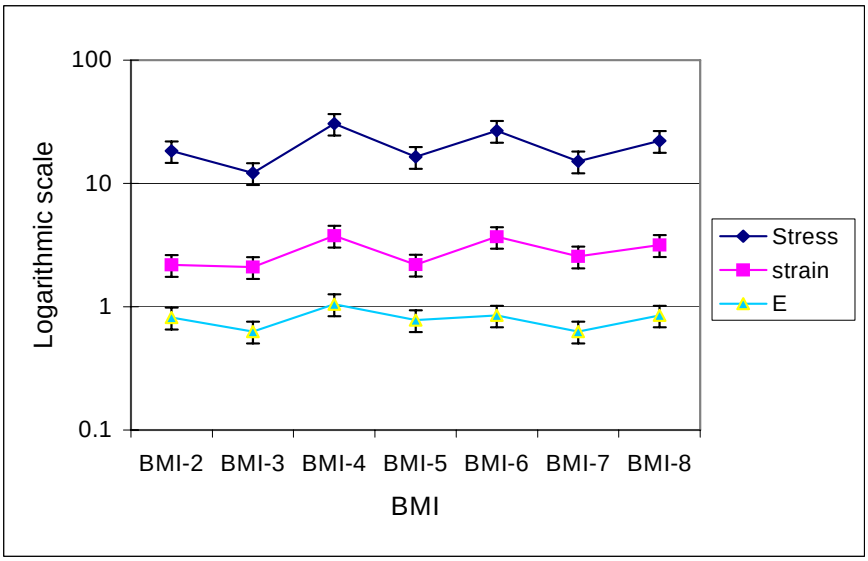


Fig. 6. The changing trends of tensile properties.

After the tensile strength reaches the maximum, the elongation at break and the tensile strength both decrease with increase of chain length. Because the chain packing gets looser with decreasing cross-linking density, the interaction of each segment gets gradually weaker and the tensile strength also gets weaker accordingly. This also shows the effect of limited elongation on the strength and Young's modulus of cross-linking networks. The results suggest that the introduction

of flexible segments into the bismaleimide molecules would actually increase the strength and flexibility of the cured resins.

Moisture absorption of BMI polymers

It is well known that moisture induces property changes in polymers. Most polymers absorb some water. Moisture absorption will increase encapsulation material's dielectric constant. Thus, lower moisture absorption is good for encapsulation materials.

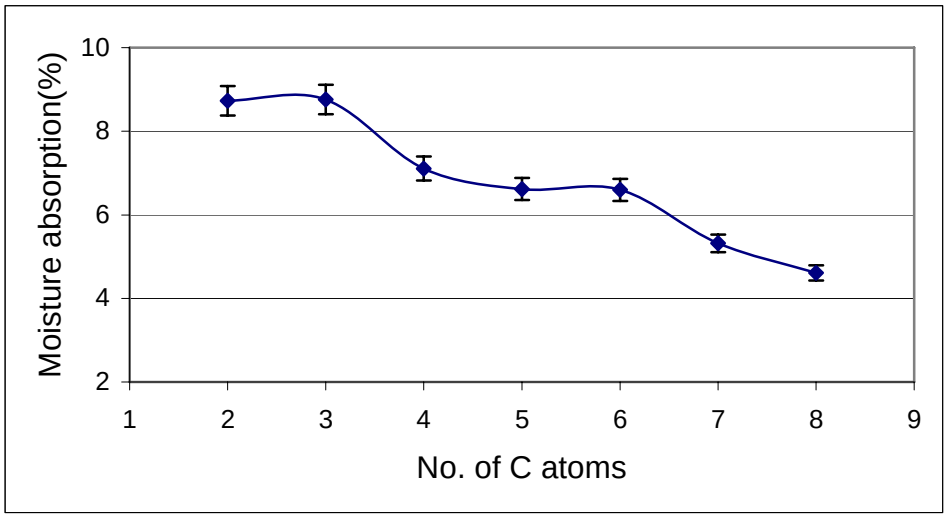


Fig. 7. Effect of chain length on the moisture absorption of BMI polymers.

Tab. 1. The molar mass of BMIs.

BMI	BMI-2	BMI-3	BMI-4	BMI-5	BMI-6	BMI-7	BMI-8
Molar mass	220.18	234.21	248.23	262.26	276.29	290.32	304.34

Figure 7 shows that moisture absorption of BMIs decreased as the chain length increased. Polymer chains with strong polar groups are able to bind water by hydrogen bridges. Some examples are the ketone group (C=O) or the sulphone group (O=S=O) and nitrogen. Imide (-CO-NH-CO-) moieties in bismaleimide are polar groups. These characteristic polar groups contain nitrogen and oxygen as potential proton acceptors to form hydrogen complexes. Water molecules close to polar groups should be able to form hydrogen-bonded complexes with nitrogen and oxygen. The amount of water molecules to be absorbed is dependent on the amount of the polar groups in the certain weight of BMI. Table 1 shows the molar mass of BMIs.

For a given weight of BMIs sample, the amount of the polar groups in BMIs should decrease as the main chain length increase. Therefore, moisture absorption of BMIs decreases with the chain length increase. This is in agreement with the experimental data in Figure 7. The decreasing moisture absorption may be also attributed to more moisture repulsive methylene group with chain length increase.

Conclusions

Thermal and tensile properties are all affected by the main chain length of BMI and odd even effect. As the chain length increases, the curing peak temperature, gel temperature of BMI all increase, but the melting point and glass transition decrease. BMI-3,5,7 have odd number of carbons so that their melting points reduced most significantly. All the BMI systems showed onsets of degradation at approximately 450°C in dry air and in pure nitrogen. The tensile properties were affected by odd even effect significantly. BMI-3,5,7 with odd number of carbons have less stress and strain than those of even ones. The moisture absorption of BMIs decreased as the chain length increased. The chain length effect and odd-even effect were studied to help understand the different effects of main chain on the properties.

Experimental part

Materials

Maleic anhydride, 1,6-hexanediamine, 1,8-diaminooctane, sodium acetate, acetic anhydride , dimethylformamide, (all from Merck™, Germany), ethylene diamine, (Fluka™) 1,3-diaminaopropane, 1,4-diaminobutane, 1,7-diaminoheptane, (all from Aldrich™, Sigma-Aldrich) and 1,5-diaminopentane, (TCI™, Japan) were used as received.

FTIR

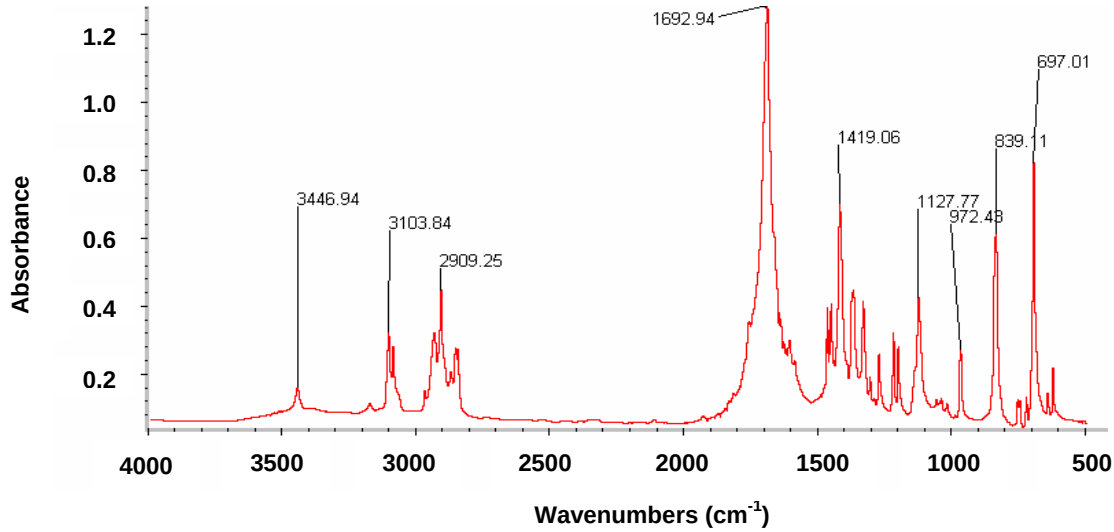


Fig. 8. FTIR spectrum of BMI-8.

FTIR analysis was carried out using a Nicolet 560 FTIR spectrometer. The typical FTIR spectrum is shown in Figure 8: the vibrations of carbonyl (C=O) absorption around 1700cm^{-1}, (-CH_2-) bands between 2880 cm^{-1} and 2980 cm^{-1}, C=C-H of maleimide ring at 3100 cm^{-1}, 825 cm^{-1}, 691 cm^{-1} [8].

Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H and ^{13}C NMR were used to obtain the chemical structure of the monomers synthesized. Samples were dissolved in deuterated solvents, $CDCl_3$, at a solid concentration of 2~10%. The NMR spectra obtained on a Bruker Spectrometer

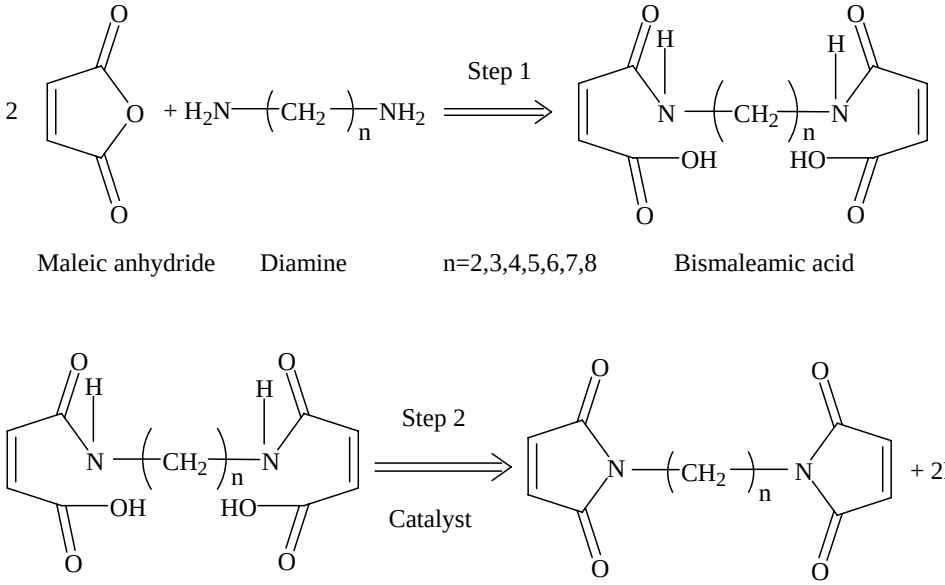
operating at 500 MHz. ^{1}H and ^{13}C NMR spectra were referenced against tetramethylsilane (TMS) at 0 ppm. The ^{13}C NMR spectra showed that the BMI compounds exhibited a carbonyl resonance around 168-170 ppm, and the maleimide double bond resonance at 133 ppm. The region of aliphatic carbons is around 0~60 ppm [2]. In the ^{1}H NMR spectra of BMI, a sharp singlet due to the proton of the double bond appeared at 6.7 ppm (4H, CH=CH) [8, 9].

Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter (DSC) TA 2920 was used to monitor the properties of the samples. About 5 mg of sample was heated from room temperature (25^{o}C) to 350^{o}C at a heating rate of 10^{o}C/min in nitrogen gas at a flow rate of 50 cm^{3}/min.

Synthesis of the BMI systems

The bismaleimides (BMI) were prepared by a two stage method [10-12] shown in Scheme 1.



Scheme 1. The formation of bismaleimides by two stage reaction.

0.0795 mol of the diamine was dissolved in 150 ml of N,N-dimethylformamide (DMF) and added in a five-necked 500ml reaction flask equipped with a stirrer, a dropping funnel, a temperature controller, nitrogen inlet and a reflux condenser. The solution containing 0.159 mol of maleic anhydride in 150 ml of N,N-dimethylformamide(DMF) was added gradually by a dropping funnel over 5 minutes at room temperature. The solution was stirred at 50 °C for 2 h without catalyst and then kept at 50 °C for 6 h under catalysts of sodium acetate and acetic anhydride. The solution was cooled to room temperature, removed most of DMF by the rotary evaporator and then added into the distilled water. The precipitate was collected, washed with $NaHCO_3$ and with distilled water for several times and dried by vacuum oven at 50°C for 48 hours. The

off-white solid was obtained. According the relative diamines, the synthesized bismaleimides were called BMI-2,3,4,5,6,7,8 and tabulated in Table 2.

Tab. 2. BMI code and its main chain.

Bismaleimides (BMI)	Main chain
BMI-2	$-(CH_2)_2-$
BMI-3	$-(CH_2)_3-$
BMI-4	$-(CH_2)_4-$
BMI-5	$-(CH_2)_5-$
BMI-6	$-(CH_2)_6-$
BMI-7	$-(CH_2)_7-$
BMI-8	$-(CH_2)_8-$

Thermogravimetric Analyzer (TGA)

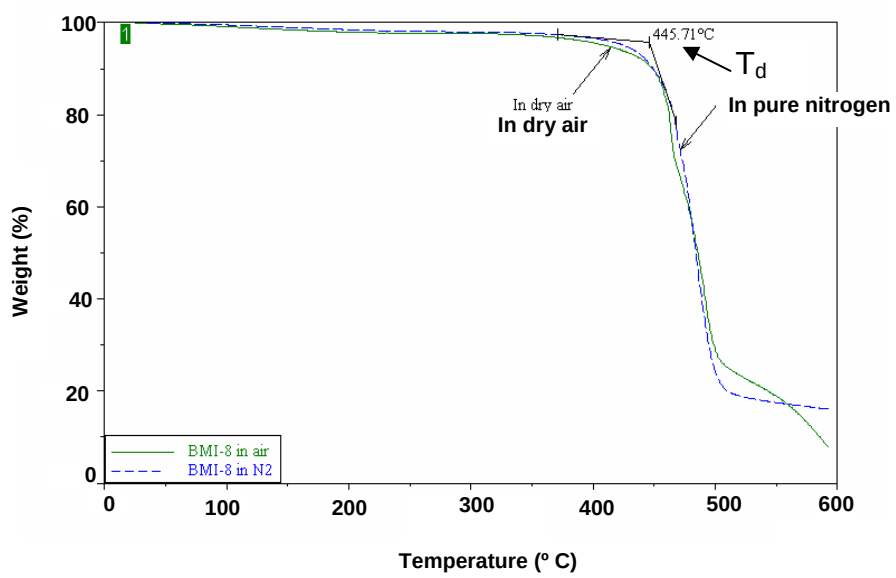


Fig. 9. Typical TGA plot of the BMI-8 polymer.

TGA analysis was carried out on a TA 2950 TGA system to determine the thermal decomposition of the bismaleimide samples. Approximately 10 mg of the sample was placed in platinum pan and then heated from room temperature (25°C) to 800 °C at a heating rate of 20° C/min. The samples were tested for their thermal stability in both dry air and purified nitrogen gas at a flow rate of 50 ml/min. The extrapolated onset decomposition temperature (T_d) was obtained from the thermogram. Figure 9 showed a TGA varying trends of a cured BMI in dry air and in pure nitrogen.

Thermomechanical Analyzer (TMA)

The coefficient of thermal expansion (CTE) and the T_g of the cured BMIs were determined using a TA 2940 TMA system. The effect of varying the chain length of the diamine on the T_g and the CTE of cured BMI samples were evaluated. The cured BMI was cut into dimensions of approximately 5mm x 5mm and 3mm (thickness) and ground to ensure surface flatness. The TMA system was fitted with a flat-bottomed quartz expansion probe. A static load of 5mN was applied on the sample and the dimensional change in the sample when heated from room temperature (25°C) to 425 °C at a heating rate of 10 °C/min was measured. The CTE values below and above the T_g of the sample, i.e. α_1 and α_2 respectively and the T_g for each of BMI type were recorded. A typical TMA thermogram of a cured BMI is shown in Figure 10.

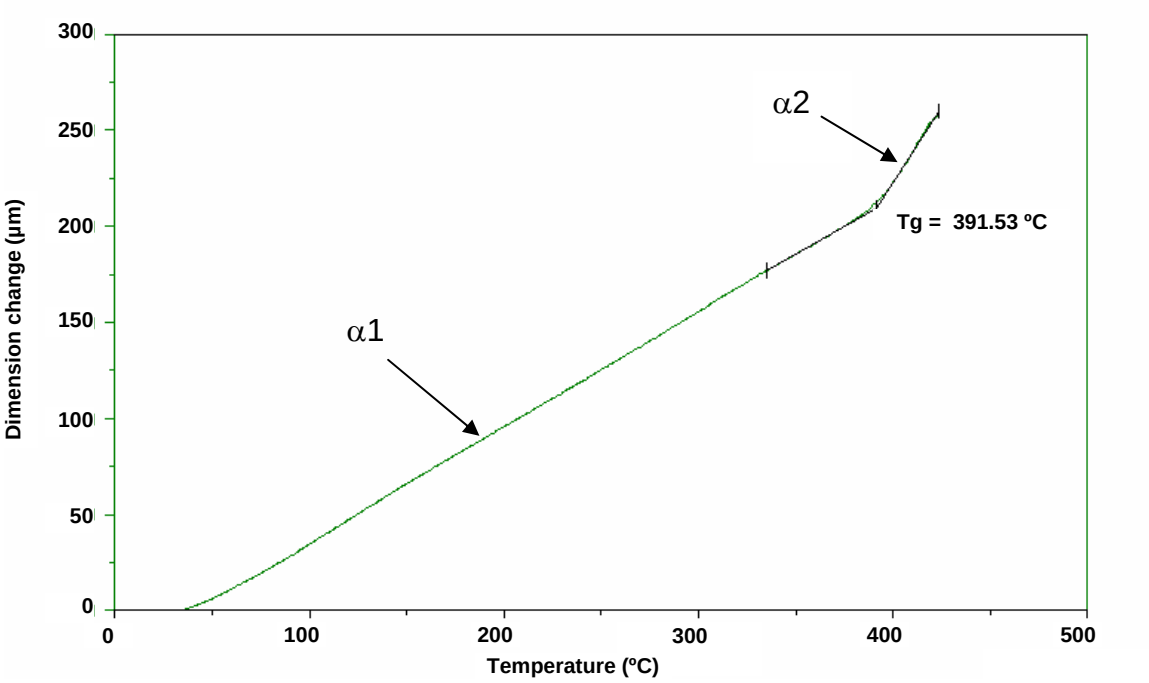


Fig. 10. Typical TMA thermogram of cured BMI.

Moisture absorption

Moisture absorption experiments were performed on thin bismaleimide films that were dried for two days at 100 °C in a vacuum oven prior to contact with water. These rectangular samples had nominal length of 30 mm, a width of 10 mm, and a thickness of 0.06 mm. This sample geometry was chosen in order to have a relatively high surface area to volume ratio to assist in the attainment of water absorption equilibrium. Absorption experiments were performed at 50 °C and were considered complete after 14 days of immersion in deionised water. At the end of the experiment, the samples were quickly removed from the water, blotted dry, and immediately weighed to determine the total water uptake.

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